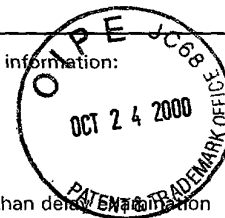
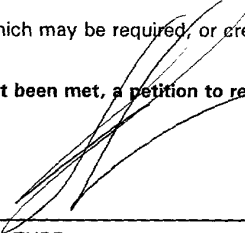


FORM-PTO-1390 (Rev. 12-29-99)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		004900-188	U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)
		09/673951	
INTERNATIONAL APPLICATION NO. PCT/FR99/00950	INTERNATIONAL FILING DATE 21 April 1999	PRIORITY DATE CLAIMED 24 April 1998	
TITLE OF INVENTION METHOD FOR PREPARING LOW VISCOSITY TRICONDENSATE POLYFUNCTIONAL ISOCYANATES			
APPLICANT(S) FOR DO/EO/US Eugenie CHARRIERE; Jean-Marie BERNARD; Denis REVELANT			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11. to 16. below concern other document(s) or information included:</p> <p>11. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A FIRST preliminary amendment.</p> <p style="margin-left: 20px;"><input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input type="checkbox"/> Other items or information:</p>			



U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) 09/673951		INTERNATIONAL APPLICATION NO. PCT/FR99/00950		ATTORNEY'S DOCKET NUMBER 004900-188	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS	PTO USE ONLY
Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 (960) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 (970) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 (958) International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 (956) International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962)					
ENTER APPROPRIATE BASIC FEE AMOUNT =					
Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$	
Claims	Number Filed	Number Extra	Rate		
Total Claims	61 -20 =	41	X\$18.00 (966)	\$	738.00
Independent Claims	XX -3 =	XX	X\$80.00 (964)	\$	640.00
Multiple dependent claim(s) (if applicable)			+ \$270.00 (968)	\$	270.00
TOTAL OF ABOVE CALCULATIONS =				\$	2,508.00
Reduction for 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	
SUBTOTAL =				\$	2,508.00
Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). 20 <input type="checkbox"/> 30 <input type="checkbox"/>				\$	
TOTAL NATIONAL FEE =				\$	2,508.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property +				\$	40.00
TOTAL FEES ENCLOSED =				\$	2,548.00
				Amount to be:	
				refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ <u>2,548.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u> . A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
Norman H. Stepno BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620			SIGNATURE  _____ Teresa Stanek Rea NAME 30,427 REGISTRATION NUMBER		

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Eugenie CHARRIERE et al.) Group Art Unit: Unassigned
Application No.: Unassigned) Examiner: Unassigned
(Corresponds to PCT/FR99/00950)
International Filing Date: 21 April 1999
For: METHOD FOR PREPARING LOW)
VISCOSITY TRICONDENSATE)
POLYFUNCTIONAL ISOCYANATES)

PRELIMINARY AMENDMENT

BOX PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

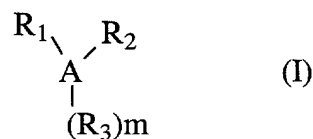
Kindly delete claims 1-23 without prejudice or disclaimer and insert the following in lieu thereof.

--24. A process for preparing a tricondensate polyfunctional isocyanate composition, comprising the step of adding to a tricondensate polyfunctional isocyanate, or to a mixture of different tricondensate polyfunctional isocyanates, obtained by (cyclo)condensation of one or more identical or different isocyanate monomers and optionally of another monomer, an allophanate of one or more identical or different isocyanates, or a mixture of different allophanates, the isocyanates or mixtures of

isocyanate monomers used to prepare the polyfunctional isocyanate(s) being identical to or different from the isocyanate(s) or the mixture of isocyanates used to prepare the allophanate(s).

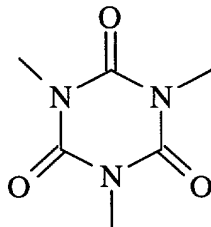
25. A process for preparing a tricondensate polyfunctional isocyanate composition, comprising at least one isocyanurate and/or biuret group, which comprises the step of adding to a tricondensate polyfunctional isocyanate, or to a mixture of different tricondensate polyfunctional isocyanates, obtained by (cyclo)trimerization of one or more identical or different isocyanate monomers and optionally of another monomer, an allophanate of one or more identical or different isocyanates, or a mixture of different allophanates, the isocyanates or mixtures of isocyanate monomers used to prepare the polyfunctional isocyanate(s) being identical to or different from the isocyanate(s) or the mixture of isocyanates used to prepare the allophanate(s).

26. The process of claim 24 or claim 25, wherein the tricondensate polyfunctional isocyanates has the following general formula:

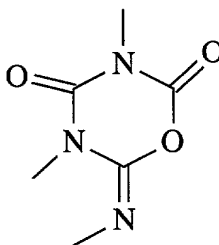


in which A represents:

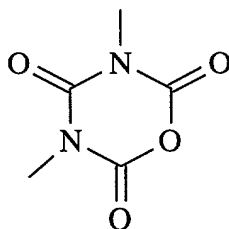
- an isocyanurate group of formula:



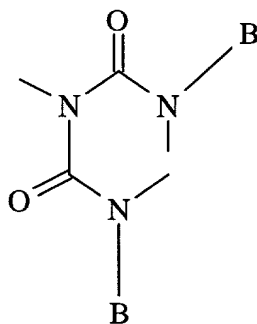
- an imino-oxadiazine-dione of the following formula:



- an oxadiazine-trione of the following formula:

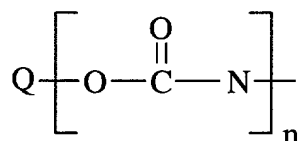


- a biuret group of formula:



B being H or a hydrocarbon-based group containing 1 to 20 carbon atoms, carbon and hydrogen as well as, optionally, other atoms (O, S, Si, etc.); or

- a group of formula:



and in which R_1 , R_2 and R_3 , which may be identical or different, represent a hydrocarbon-based group, comprising a true or derived isocyanate function,

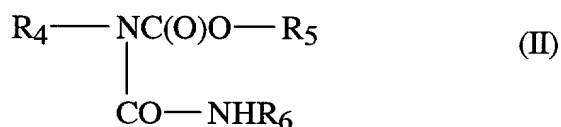
Q is a hydrocarbon-based group, as defined for R_1 to R_3 ,

m is an integer from 0 to 2,

n is the integer 3 or 4.

27. The process of claim 24 or claim 25, wherein the tricondensate polyfunctional isocyanate composition comprises at least one true isocyanurate polyisocyanate.

28. The process of claim 24 or claim 25, wherein the allophanates or of the following formula II:



in which:

- R_4 and R_6 , which may be identical or different, represent a hydrocarbon-based group comprising a true or derived isocyanate function,
- R_5 represents an alkyl group.

29. The process of claim 24 or claim 25, wherein a mixture of allophanates, is added to the tricondensate polyfunctional isocyanates.

30. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and trisallophanates, in an amount of at least 2/3, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

31. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and trisallophanates, in an amount of at least 75%, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

32. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and tris-allophanates, in an amount of at least 90%, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

33. The process of claim 24 or claim 25, wherein the amount of bis-allophanate represents up to 10% of the total weight of the allophanate composition.

34. The process according to claim 24 or claim 25, wherein the amount of tris-allophanates is less than or equal to 30%, relative to the total weight of the composition.

35. The process according to claim 24 or claim 25, wherein the amount of tris-allophanates is less than or equal to 20%, relative to the total weight of the composition.

36. The process according to claim 24 or claim 25, wherein the amount of tris-allophanates is less than or equal to 15%, relative to the total weight of the composition.

37. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and tris-allophanates and the ratio bis-allophanate functions + tris-allophanate functions/mono-allophanate functions is equal to or greater than 0.1.

38. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and tris-allophanates and the ratio bis-allophanate functions + tris-allophanate functions/mono-allophanate functions is equal to or greater than 0.3.

39. The process of claim 24 or claim 25, wherein the mixture of allophanates comprises mono-, bis- and tris-allophanates and the ratio bis-allophanate functions + tris-allophanate functions/mono-allophanate functions is equal to or greater than 0.5.

40. A process for preparing a low-viscosity tricondensate polyfunctional isocyanate composition, comprising the following steps a) and b) in any order:

a) (cyclo)condensating, in the presence of a catalyst, of one or more identical or different first isocyanate monomer(s) until the desired degree of conversion is obtained;

b) reacting one or more second isocyanate monomer(s) which are identical to or different from one another and identical to or different from the first isocyanate monomer(s), with an alcohol to form a carbamate, the reaction optionally being catalyzed, and simultaneous or subsequent reaction of the carbamate with one or more isocyanate

monomer(s) which are identical to or different from the previous monomers, to give an allophanate or mixture of allophanates;
and steps c) and d) in any order:

- c) mixing the reaction product from step a) with all or some of the reaction product from step b) and optionally
- d) removing the isocyanate monomers.

41. The process of claim 24 or 40, wherein the isocyanate(s) used for the (cyclo)condensation reaction is (are) identical to the isocyanate(s) used for the allophanatation reaction.

42. The process of claim 24 or 40, wherein the isocyanate(s) used for the allophanatation reaction and the isocyanate(s) used for the cyclotrimerization reaction satisfy one, two or three of the following conditions:

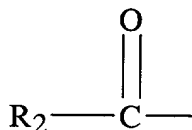
- at least one or at least two, of the NCO functions are linked to a hydrocarbon-based skeleton via a saturated (sp^3) carbon;
- at least one or at least two, of said saturated (sp^3) carbons bears at least one, respectively two, hydrogen(s)
- all the intermediate carbons via which the isocyanate functions are linked to the hydrocarbon-based skeleton are saturated (sp^3) carbons which partially, or totally, bear one hydrogen or two hydrogens.

43. The process of claim 40, wherein the alcohol is selected from the group consisting of:

- aliphatic monoalcohols containing a C₁-C₁₀ linear chain;
- aliphatic monoalcohols containing a C₃-C₁₂ branch chain comprising not more than four secondary carbon atoms;

- diols containing a linear C₂-C₄₀ or branched C₃-C₄₀ chain;

of formula R- [O-CH(R₁) -CH₂]_n-OH, in which R₁ represents H or a C₁-C₈ alkyl group, or polyether of formula -CH₂OR₁₀, R₁₀ representing a polyoxyalkylene chain, n is an integer from 1 to 50, and R is a linear or branched C₁-C₂₀ alkyl group, or R is a group



with R₂ being a linear or branched C₁-C₂₀ alkyl group; and

- silanols.

44. The process of claim 40, wherein the NCO/OH ratio of respectively the isocyanate and the alcohol in step b) is greater than 4.

45. The process of claim 40, wherein at least about 25% by weight of the product from step b) is mixed with product from step a).

46. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 10% of tricondensate allophanates relative to the total weight of the composition.

47. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 8% of tricondensate allophanates relative to the total weight of the composition.

48. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 5% of tricondensate allophanates relative to the total weight of the composition.

49. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 4% of tricondensate allophanates relative to the total weight of the composition.

50. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one

primary allophanate, said composition comprising less than 3 % of tricondensate allophanates relative to the total weight of the composition.

51. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 2 % of tricondensate allophanates relative to the total weight of the composition.

52. A reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, said composition comprising less than 1 % of tricondensate allophanates relative to the total weight of the composition.

53. A reduced-viscosity tricondensate polyfunctional isocyanate composition, comprising at least one true tricondensate polyfunctional isocyanate and at least one allophanate, said composition satisfying at least one, advantageously two, of the following conditions:

- a G ratio defined by:

True tricondensate polyisocyanates, obtained from the condensation of three identical or different isocyanate molecules not modified with carbamate or allophanate

G= _____

Sum of the polyisocyanate molecules bearing at least one tricondensate function
obtained from the condensation of three identical or different isocyanate molecules
greater than 0.3,

- an allophanate/allophanate + true trimer weight ratio of between 2.5% and 99%,
- the tricondensates are obtained from a tricondensation reaction for which the degree of conversion of the identical or different isocyanate monomer(s) into tricondensate polyfunctional polyisocyanates contained in the composition is greater than 8%,
- at least 1% and not more than 99%, of biuret is present, these amounts being given on a weight basis.

54. The tricondensate polyfunctional isocyanate composition of claims 46 or 53, wherein the mixture of allophanates comprises mono-, bis- and tris-allophanates in an amount of at least 2/3, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

55. The tricondensate polyfunctional isocyanate composition of claims 46 or 53, comprising an amount of his-allophanate representing up to 10%, of the total weight of the allophanate composition.

56. The tricondensate polyfunctional isocyanate composition of claims 46 or 53, comprising an amount of tris-allophanates less than or equal to 30%, by weight relative to the total weight of the composition.

57. The tricondensate polyfunctional isocyanate composition of claims 46 to 53, comprising a ratio bis-allophanate functions + tris-allophanate functions/monoallophanate functions greater than or equal to 0.1, and up to 0.3.

58. The tricondensate polyfunctional isocyanate composition of claim 46, comprising hexamethylene diisocyanate biuret.--

REMARKS

Entry of the foregoing amendment(s) is respectfully requested.

The claims have been amended to place them in better condition for U.S. patent practice.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

Teresa Stanek Rea
Registration No. 30,427

P.O. Box 1404
Alexandria, Virginia 22313-1404
(703) 836-6620

Date: October 24, 2000

Process for preparing low-viscosity tricondensate
polyfunctional isocyanates.

The invention relates to the preparation of reduced-viscosity polyisocyanate compositions which are intended in particular for two-component coating compositions, in particular paints.

Polyisocyanates are widely used in the coating industry, in particular in paints, on account of their many properties. In particular, it is known practice to use, as hardeners, polyisocyanates comprising isocyanurate groups on account of their crosslinking ability.

However, the compositions of this type obtained by trimerization of an isocyanate have a relatively high viscosity, making it necessary to use a substantial amount of solvent.

In point of fact, new regulations regarding environmental control demand a reduction in volatile organic compounds.

To satisfy these requirements, one of the possibilities consists in limiting the degree of conversion of the starting isocyanates, in particular of the diisocyanates, in order to minimize the formation of heavy compounds (polycondensates with a higher degree of polymerization, more particularly comprising more than one trimer unit) which are present in the trimerization medium and which are responsible for increasing the viscosity. To this end, the amount of catalyst is reduced for a fixed reaction time, or the duration of reaction is reduced for a given amount of catalyst, in order to increase the true cyclotrimer/heavy compound ratio.

The Applicant already markets products of this type, HDT (Hexamethylene Diisocyanate Trimer) and HDB (Hexamethylene Diisocyanate Biuret), which are referred to by the abbreviation LV meaning "Low Viscosity".

The drawbacks of these procedures are, in the first

case, a large reduction in production efficiency and, in the second case, an increase in the cost due to the amount of catalyst used for a given amount of isocyanurates.

European patent applications EP 524 500 and
5 EP 524 501 have also proposed carrying out an allophanatation reaction on a trimerization mixture or carrying out the trimerization in the presence of alcohols, which gives polyisocyanate mixtures containing isocyanurate functions, that are claimed as having a low viscosity.

10 Moreover, the fact that the viscosity of biuret compounds can be reduced by adding allophanates, or even by concomitant or consecutive allophanatation was not described.

The allophanates are obtained in the reaction
15 medium by reacting a compound containing an alcohol function with an isocyanate, followed by reacting the carbamate function thus obtained with a new isocyanate molecule simultaneously or even consecutively with the trimerization reaction.

20 The processes for obtaining polyisocyanate compositions containing isocyanurate units having a significant content of allophanate functions have hitherto consisted in subjecting the trimerization mixture obtained after partial catalytic cyclotrimerization of the starting
25 isocyanates to a consecutive allophanatation reaction in the presence of an alcohol, in particular butanol, followed by subsequent removal of the starting isocyanates by distillation under vacuum.

The compositions obtained according to the
30 processes described in the patent applications mentioned above generally have a viscosity which is somewhat lower than that of compositions not comprising allophanates.

In the course of the study which led to the present
35 invention, it has been shown, surprisingly, that it is possible to obtain a reduced viscosity for compositions

with the same content of trifunctional (poly)isocyanates, in particular trimers (comprising at least one isocyanurate and/or biuret group). Thus, compared with isocyanurate (poly)isocyanate compositions comprising allophanates of the prior art, carrying out the catalytic (cyclo)trimerization reaction and the allophanatation reaction separately leads to a significantly reduced viscosity.

It has been demonstrated that the presence of polyfunctional isocyanate allophanates (having a functionality of at least three), in particular of allophanates containing isocyanurate groups in the final composition obtained according to the methods of the prior art, significantly and adversely increases the viscosity of this composition and that, in contrast, by working such that no polyfunctional isocyanate allophanates are formed, the viscosity of the final composition is significantly lower than the viscosity of the polyfunctional isocyanate composition obtained after trimerization of the starting isocyanates.

In the text hereinbelow the expression "comprising isocyanurate groups" will be used as a paradigm for polyfunctional compounds.

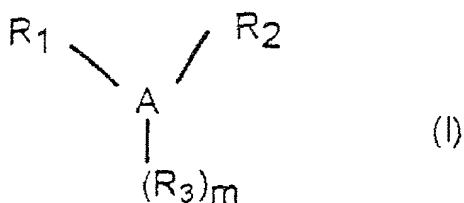
The aim of the invention is thus to provide polyfunctional isocyanate compositions comprising tricondensates preferably containing a biuret and/or isocyanurate function, the said composition comprising compounds containing allophanate functions and having a significantly reduced viscosity, preferably of at least about $1/4$, advantageously about $1/3$, even more advantageously of about $2/5$, in the absence of solvent, compared with the same composition comprising no compounds containing allophanate functions, for a given temperature.

In the present description, the term "about" means that the value given corresponds to a mathematical round-up

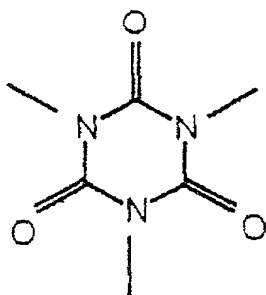
and that any zeros furthest to the right are positional zeros rather than significant figures.

To this end, one subject of the invention is a process for preparing a tricondensate polyfunctional isocyanate composition, preferably comprising at least one isocyanurate and/or biuret group, which consists in adding to a tricondensate polyfunctional isocyanate, or to a mixture of different tricondensate polyfunctional isocyanates, obtained by (cyclo)condensation, in particular (cyclo)trimerization of one or more identical or different isocyanate monomers and optionally of another monomer, an allophanate of one or more identical or different isocyanates, or a mixture of different allophanates, the isocyanates or mixtures of isocyanate monomers used to prepare the polyfunctional isocyanate(s) being identical to or different from the isocyanate(s) or the mixture of isocyanates used to prepare the allophanate(s).

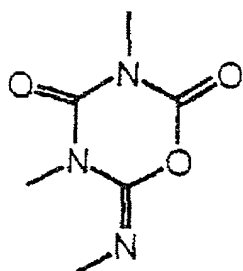
The (cyclo)tricondensate polyfunctional isocyanates of the invention correspond to the following general formula:



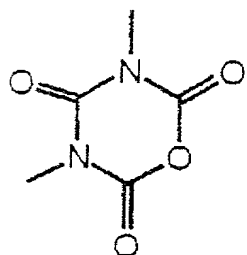
in which A represents
- an isocyanurate group of formula



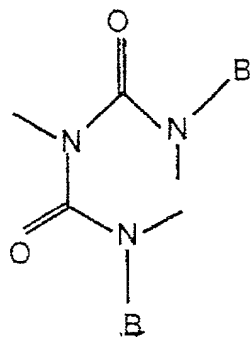
- one of its derivatives containing an imino-oxadiazine-dione skeleton of the following general formula:



- one of its derivatives containing an oxadiazine-trione skeleton of the following general formula

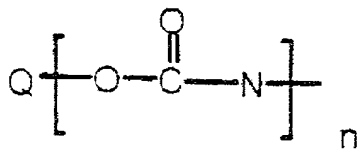


- a biuret group of formula



B being H or a hydrocarbon-based group, i.e. containing carbon and hydrogen as well as, optionally, other atoms (O, S, Si, etc.) preferably containing 1 to 20 carbon atoms; or

- a group of formula:



and in which R_1 , R_2 and R_3 , which may be identical or different, represent a hydrocarbon-based group, in particular an aliphatic, cycloaliphatic, heterocyclic or aromatic group, comprising a true or derived isocyanate function,

Q is a hydrocarbon-based group, preferably alkyl, as defined for R_1 to R_3 ,

m is an integer from 0 to 2, and

n is the integer 3 or 4.

The expression "derived isocyanate function" means carbamate, urea, biuret, urethane, uretinedione, isocyanurate and masked isocyanate functions.

The tricondensate polyfunctional isocyanates can be homotrichondensates (when R_1 , R_2 and R_3 are identical) or heterotrichondensates (when at least one from among R_1 , R_2 and R_3 is different from the others).

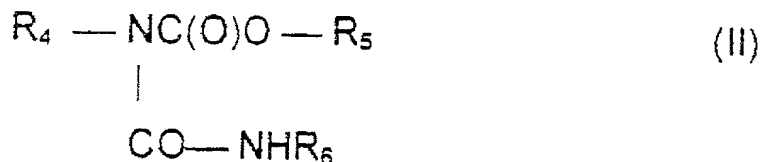
The tricondensate polyfunctional isocyanate mixtures are defined as being a combination of different homotrichondensate polyfunctional isocyanates, different heterotrichondensate polyfunctional isocyanates or a mixture of the two categories.

The expression "true tricondensate polyfunctional isocyanate" will be used when R_1 , R_2 and R_3 , which may be identical or different, represent a group -A-X, A being a hydrocarbon-based chain as defined above, i.e. comprising at least carbon and hydrogen, and X being a hydrogen atom or an NCO group.

X preferably represents an NCO group.

In other words, the expression "true tricondensate polyfunctional isocyanate" means theoretical (cyclo)condensation products obtained by condensing three moles of monomers, advantageously of isocyanates, preferably diisocyanates or even triisocyanates (which may be identical or different), with the exception of compounds derived from the condensation of more than four monomers and/or comprising allophanate groups, as well as isocyanurate oligomers obtained by oligomerization of isocyanurate (poly)isocyanates.

The allophanates of the present invention correspond to the general formula II:



in which:

- R_4 and R_6 , which may be identical or different, represent a hydrocarbon-based group, in particular an aliphatic, cycloaliphatic, heterocyclic or aromatic group, as defined above, comprising a true or derived isocyanate function,

- R_5 representing an alkyl group, i.e. the residue of an alcohol compound after removal of the OH function.

In this case, the expression "derived isocyanate function" means carbamate, urea, biuret, urethane, uretinedione, masked isocyanate and allophanate functions, with the exclusion of the isocyanurate function.

When R_4 is identical to R_6 , the term "homo-allophanates" will be used, these being obtained by condensing, onto a carbamate formed by reaction of an isocyanate of formula R_4NCO with an alcohol of formula R_5OH , a second isocyanate of formula R_6NCO , R_6 being identical to R_4 .

The allophanates can also be obtained by condensing, onto the carbamate, a second isocyanate R_6NCO , R_6 being different from R_4 , in which case the term "hetero-allophanates" will be used.

Advantageously, a mixture of allophanates comprising at least 1/4, advantageously at least 1/3 and preferably at least 2/5 (by mass) of primary allophanate(s), advantageously of a monoalcohol, is added.

The mixture can also comprise bis-allophanates, tris-allophanates and heavy allophanates, as well as smaller proportions of the carbamate of the isocyanate(s) (R_4NCO and/or R_6NCO) and of alcohol (R_5OH).

It is very desirable that the mixture should comprise at least 1/2 (by mass), advantageously not more than 1/3, preferably 1/6, of heavy allophanates (comprising more than two allophanate functions).

It should be pointed out that the bis-allophanates and tris-allophanates, in particular the bis-allophanates and tris-allophanates of monoalcohols, when added to tricondensate polyfunctional polyisocyanates as thinners, are not generally a cause of a significant increase in viscosity, unlike heavy allophanates.

The bis-allophanates and tris-allophanates even

contribute towards the thinning properties of the mono-allophanate.

5 In the context of the invention, an allophanate composition comprising solely bis-allophanates and tris-allophanates can be added to the tricondensate polyfunctional isocyanate composition.

However, this embodiment is not preferred on account of the difficulty in preparing a composition free of mono-allophanate.

10 Thus, in the case of a monofunctional alcohol in particular, the sum of the mono-, bis- and tris-allophanates added as thinners to the tricondensate polyfunctional isocyanate composition is advantageously at least 2/3 and preferably at least 75%, preferably at least
15 90%, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

The amount of bis-allophanates can be up to 10% or even 20% by weight relative to the total weight of the
20 allophanate composition without substantially modifying the thinning properties of this composition.

In parallel, the amount of tris-allophanates can represent up to 30% by weight relative to the total weight of the allophanate composition. However, this amount
25 preferably does not exceed 20%, and preferentially 15%, by weight.

The allophanate composition added to the tricondensate polyfunctional isocyanate composition still has very good thinning properties when the ratio
30
$$\frac{\text{bis-allophanate functions} + \text{tris-allophanate functions}}{\text{mono-allophanate functions}}$$
 is greater than or equal to 0.1, and can be up to 0.3 or even 0.5.

35 Given that the (poly)isocyanate composition to be thinned contains only a small amount of allophanates, the

above characteristics are found in the ratios between allophanates of the final mixture.

Depending on the viscosity of the composition to be thinned, an allophanate composition should be used whose viscosity at 25°C is not more than 45%, advantageously 35%, preferably 30%, of the viscosity of the (poly)isocyanate composition to be thinned.

The term "primary" allophanate means the theoretical molecular reaction product expected from the reaction between the isocyanate(s) and the alcohol corresponding to the product of reaction of two moles of isocyanate function per mole of alcohol function.

In the case of diols, the primary allophanate is the product of reaction of four moles of isocyanates with one mole of diol. This is thus a di-allophanate which must be distinguished from bis-allophanates and higher homologues, which are the products of oligomerization of primary allophanates.

The primary allophanate is obtained from a single alcohol molecule bearing one or more hydroxyl functions converted into allophanate functions.

Thus, the allophanate is true when the following condition is met:

Total number of allophanate functions per molecule of compound bearing allophanate functions

= 1/2

Number of identical or different isocyanate chains engaged in the allophanate functions borne by the compound molecule which bear allophanate functions.

The term "mono-allophanate" means the theoretical reaction product from reacting one mole of isocyanate R_4NCO with one mole of alcohol (R_5OH) and of one mole of isocyanate R_6NCO with the carbamate function thus formed.

A bis-allophanate is a molecule which is characterized by the fact that it comprises two allophanate functions, separated by an at least partially hydrocarbon-based chain.

5 In the case of these molecules, the ratio indicated above is greater than 1/2, the calculation of this ratio not taking into account the allophanate molecules containing carbamate functions.

10 When the starting isocyanates are diisocyanates, the bis-allophanates are obtained either from monoalcohols or from diols.

15 In the case of monoalcohols, the bis-allophanate molecule comprises 3 isocyanate monomers and 2 alcohol molecules. In the case of diols, the bis-allophanate molecule comprises 4 isocyanate molecules.

The bis-allophanates obtained from a diol are less thinning than those obtained from the double attack of a monoalcohol, but can raise the content of isocyanate functions and provide a greater crosslinking effect.

20 The tris-allophanates are defined in the same way as the bis-allophanates.

25 When the allophanates are synthesized from several alcohols comprising diols, it is preferable to start by synthesizing the bis-allophanates obtained from diols in order to avoid their polycondensation.

30 In addition, according to the invention, a combination of different homoallophanates, of different heteroallophanates or a mixture of these two categories, or alternatively a mixture of homoallophanates and/or of heteroallophanates obtained with different alcohols, can also be added to the tricondensate polyfunctional isocyanates.

35 The term "heavy" condensate compounds means those obtained by reacting more than four monomers with one another.

The term "heavy allophanates" means the allophanate products which do not fall into any of the categories previously defined.

In particular, allophanates comprising a derived isocyanate function (biuret and/or isocyanurate) and at least one allophanate function and compounds comprising at least three allophanate functions, which are also known as tricondensate allophanates, fall within the category of heavy allophanates.

The present invention is not limited to the nature of the isocyanate monomers used. Thus, the isocyanate monomers can be aliphatic, including cycloaliphatic and arylaliphatic, mono- advantageously di- or triisocyanates, preferably diisocyanates, such as:

- polymethylene diisocyanates and in particular hexamethylene diisocyanate, 2-methyl pentamethylene diisocyanate, 4-isocyanatomethyl octamethylene diisocyanate or 2,4,4-trimethyl hexamethylene diisocyanate;

- isophorone diisocyanate, norbornane diisocyanate, 1,3-bis(isocyanatomethyl)cyclohexane (BIC), H₁₂-MDI and cyclohexyl 1,4-diisocyanate;

- arylenedialkylene diisocyanates (such as OCN-(CH₂)_p-Ø-(CH₂)_q-NCO), p and q being identical or different integers between 1 and 6, preferably 2 and 4;

- or alternatively aromatic isocyanates such as tolylene diisocyanate.

The aromatic isocyanates and the isocyanates whose isocyanate function is borne by a neopentyl carbon are not preferred.

The preferred isocyanates targeted by the invention are those in which at least one, advantageously two, preferably three, of the following conditions are met:

- at least one, advantageously two, of the NCO functions are linked to a hydrocarbon-based skeleton via a saturated (sp³) carbon;

- at least one, advantageously two, of the said saturated (sp^3) carbons bears at least one, advantageously two, hydrogen(s). In other words, it has been found that better results are obtained when the carbon bearing the isocyanate function bears a hydrogen, preferably two hydrogens. It is also even preferable for at least a third, advantageously at least a half, preferably at least two thirds, of the said saturated (sp^3) carbons to be linked to the said skeleton via a carbon atom which itself bears at least one hydrogen, more preferably two;

- all the intermediate carbons via which the isocyanate functions are linked to the hydrocarbon-based skeleton are saturated (sp^3) carbons which advantageously partially, preferably totally, bear a hydrogen, preferably two hydrogens. It is also even preferable that at least a third, advantageously at least a half, preferably at least two thirds, of the said saturated (sp^3) carbons are linked to the said skeleton via a carbon atom which itself bears at least one hydrogen, more preferably two.

In general, the preferred starting isocyanates (monomers) are those comprising at least one polymethylene chain (comprising from 2 to 6 methylene chain units).

The preferred isocyanates, in particular aliphatic diisocyanates, especially C_1 - C_{10} alkyl isocyanates, are those in which the alkyl chain is linear or weakly branched. The expression "weak branching" means the absence of tertiary and neopentyl carbons.

HDI, IPDI, NBDI, H_{12} -MDI and MPDI are particularly preferred.

In general, since aliphatic isocyanates generally speaking have a lower viscosity than cycloaliphatic isocyanates, it will be preferred to avoid the use of isocyanate allophanates containing cycloaliphatic functions when the desired effect is to reduce the viscosity of the isocyanurate (poly)isocyanates obtained from isocyanates

containing aliphatic functions.

In general, in order to obtain a relatively significant reduction in the level of viscosity, the mixture needs to be such that it has a viscosity which is lower than that of the initial mixture, free of monomers and solvents, i.e. by at least about 1/4, preferably by at least about 1/3 and advantageously by at least about 2/5, compared with that of the initial mixture without allophanates.

A subject of the invention is, more particularly, a process for preparing a reduced-viscosity tricondensate polyfunctional isocyanate composition from isocyanates, comprising the following steps a) and b) in any order:

a) (cyclo)condensation, in the presence of a catalyst, of one or more identical or different first isocyanate monomer(s) until the desired degree of conversion is obtained;

b) reaction of one or more second isocyanate monomer(s) which are identical to or different from one another and identical to or different from the first isocyanate monomer(s), with an alcohol to form a carbamate, the reaction optionally being catalyzed, and simultaneous or subsequent reaction of the carbamate with one or more isocyanate monomer(s) which are identical to or different from the previous monomers, to give an allophanate or mixture of allophanates;

and steps c) and d) in any order:

c) mixing the reaction product from step a) with all or some of the reaction product from step b); and optionally

d) removing the isocyanate monomers.

The (cyclo)condensation reaction is advantageously a (cyclo)trimerization reaction, which is carried out in the presence of a (cyclo)trimerization catalyst that is known per se.

When a catalyst is used for the carbamatation reaction, the same catalyst will advantageously be used for the allophanatation reaction. However, different catalysts may be used.

5 The carbamatation and allophanatation reactions can be carried out in two stages, for example by increasing the temperature of the reaction medium until the carbamatation reaction takes place, and subsequently increasing the temperature until the allophanatation reaction takes place.

10 The two reactions can also take place simultaneously by increasing the reaction temperature directly up to the allophanatation temperature.

 It is possible to use in steps a) and b) of the process the same isocyanate monomer(s) which will then be
15 subjected in parallel to a catalytic trimerization and a carbamatation reaction followed by an allophanatation reaction, the optionally purified reaction media then being mixed until the desired viscosity is obtained.

 In order to reduce the viscosity of a tricondensate
20 polyfunctional isocyanate of a higher alkyl (containing more than 10 carbon atoms) which is optionally branched, cycloalkyl or aromatic and which thus has a higher viscosity than that of a lower alkyl polyisocyanate (containing not more than 10 carbon atoms), it is also
25 possible to add to the trimerization product the product obtained after carbamatation and allophanatation of one or more isocyanate(s) different from the first isocyanate(s) and having a lower viscosity than that which would be obtained by carbamatation and then allophanatation of the
30 first isocyanate(s).

 To this end, the isocyanate(s) used for the carbamatation/allophanatation reactions will advantageously be one or more linear alkyl isocyanate(s), in particular HDI.

35 Step a) is carried out under the usual conditions

for the catalytic trimerization of isocyanates.

Mention may be made, by way of example, in the case of the tricondensates containing isocyanate functions, of the conventional reaction of HDI by catalysis in the presence of an aminosilyl derivative, in particular a silane or a disilazane, preferably hexamethyldisilazane (HMDZ) as described in EP 57 653 or in the presence of a quaternary ammonium catalyst.

The reaction conditions comprise, in particular for a reaction catalyzed with HMDZ, an amount of catalyst of the order of 1.2% by weight relative to the weight of the HDI, a reaction time of about 2 h 30 minutes and a temperature of about 120°C.

Under these conditions, the degree of conversion of the isocyanate functions is 32.7%, which corresponds to the production of an isocyanurate (poly)isocyanate mixture whose content of true HDI trimer functions (comprising a single isocyanurate ring) is about 50% by weight.

Mention may also be made of reactions catalyzed with carboxylic acids in the presence of water in order to obtain condensates containing biuret units (patent FR 86/12524).

Step b) comprises a conventional carbamatation reaction followed by a conventional allophanatation reaction, the two reactions possibly being catalyzed with the same catalyst or a combination of catalysts, and the two reactions possibly proceeding simultaneously in a single reactor.

In a first stage, the isocyanate(s) used for the allophanatation reaction, which may be identical to or different from the isocyanate(s) used for the (cyclo)condensation reaction, advantageously the (cyclo)trimerization reaction, is (are) optionally reacted in the presence of an allophanatation catalyst with one or more compounds comprising at least one alcohol function.

The reaction is carried out at a temperature which is advantageously from about 80°C to about 100°C, when the carbamatation and allophanatation reactions are carried out in two stages, or directly at a temperature of about 100°C to 180°C when the carbamatation and allophanatation reactions are carried out simultaneously.

An alcohol containing an aliphatic chain, including alcohols containing a cycloaliphatic chain or, preferably, an alcohol containing a linear or weakly branched alkyl chain, comprising only one OH function is advantageously used. Mention may be made in particular of alkyl alcohols containing a linear C₁-C₁₀ chain, C₄-C₈ alcohols being preferred.

The weakly branched aliphatic alcohols are, in particular, C₃-C₂₀ aliphatic alcohols comprising at least one and preferably not more than four secondary carbon atoms. Mention may be made in particular of primary alcohols containing an ethylhexyl chain, in particular a 2-ethylhexyl chain.

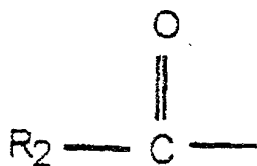
Suitable alcohols can also optionally comprise one or more double bonds.

The compound comprising at least one alcohol function can also comprise one or more other functions, such as cetone, nitrile, ester, ether or polyether (in particular polyethylene oxide monoether advantageously comprising not more than 20 and preferably not more than 10 polyethylene oxide chain units), siloxane (US-A-6 536 556) or fluoro (JP 81-49329).

Diols, in particular C₂-C₄₀ diols containing a linear or branched alkyl chain as defined above for the monoalcohols, can also be used. However, these generally give products of substantially higher viscosity than their monohydroxylated homologues and are generally used as a mixture with monoalcohols only when a crosslinking effect rather than a chain-extending effect is desired.

The alcohol compound can be a polyester or acrylic oligomer such as, for example, the commercial derivatives K Flex 188 or oligomers derived from castor oil such as the commercial products CASPOL 1842, 5001, 5003, 5007, 5002, etc.

Other alcohols that are particularly advantageous from the point of view of low viscosity are monoalcohol esters and/or ethers, in particular the compounds of formula $R-[O-CH(R_1)-CH_2]_n-OH$, in which R_1 represents H or an alkyl group, preferably a C_1-C_8 alkyl group, in particular methyl, or polyether, in particular $-CH_2OR_{10}$, R_{10} representing a hydrocarbon-based chain as defined above, in particular polyoxyalkylene, preferably polyoxyethylene, n is an integer preferably from 1 to 50, and R is a linear or branched C_1-C_{20} alkyl group, or R is a group



with R_2 being a linear or branched C_1-C_{20} alkyl group.

As mentioned above, the aliphatic chain of the compound comprising at least one OH function can also be substituted or interrupted with a cycloalkyl or heterocyclic group.

The OH function can be linked directly to a carbon atom of a hydrocarbon-based ring or of the heterocycle.

Silanol-type derivatives are also suitable.

The reaction is generally continued until an NCO content corresponding to the consumption of at least 80% of the alcohol functions is obtained.

A mixture of compounds containing different alcohol function(s) can also be added during the carbamatation/allophanatation reaction.

When the actual carbamatation and allophanatation reactions are dissociated, it is possible, after carbamatation, in a second stage, to raise the temperature of the reaction medium up to about 100°C-180°C, preferably in the region of 140°C for HDI, in order to carry out the allophanatation reaction, this reaction optionally being carried out in the presence of an allophanatation catalyst, in particular a catalyst based on tin, zinc or other metals known to those skilled in the art. Mention may be made in particular of dibutyltin dilaurate (DBTL), tin bis(2-ethyl hexanoate) and tin dichloride, DBTL being preferred.

The amounts of catalyst are advantageously between 0.001% and 0.1%, in particularly 0.001% and 0.05%, preferably about 0.005% by weight of metal relative to the weight of isocyanate(s).

The reaction time is advantageously from about 1 to 24 hours, preferably between 3 and 7 hours.

The allophanatation reaction is carried out so as to predominantly obtain primary allophanates, as defined above.

An isocyanate different from the one used in the carbamatation reaction can be used. In this case, a mixed allophanate is obtained.

In order to predominantly obtain primary allophanates, the isocyanate (NCO) functions/hydroxyl (OH) functions ratio is advantageously high. A ratio of greater than 4 and better still greater than 6 will preferably be used, a ratio of about 8 being particularly advantageous.

In the case of difunctional or polyfunctional alcohols, an (NCO)/OH ratio of greater than 10 is more advantageous.

When the NCO/OH ratio is low, the viscosity of the final product is high on account of the significantly higher presence of heavy allophanates such as the bis-allophanate oligomers or higher homologues. Thus, the

viscosity of the HDI butyl allophanate is multiplied by 4 when the NCO/OH ratio is reduced from 8 to 4.

The reactions of step a) and of step b) are monitored by measuring the NCO titres.

5 Step c) is carried out by mixing the products from steps a) and b) in proportions varying as a function of the desired final viscosity, in accordance with the empirical law given by the formula:

$$\text{Log } \eta_{\text{mixture}} = \text{Sum } x_i \text{ Log } \eta_i$$

10

with η being the viscosity of the product or of the mixture and x being the mass fraction of the products in the mixture.

15 This law makes it possible to evaluate the amount of allophanate(s) which should be added to a polyisocyanate composition to be thinned as a function of the viscosity which it is desired to obtain.

20 In the course of the present invention, it has been demonstrated, surprisingly, that, although the compositions to be mixed together are of different structure and different molecular mass, they satisfy this law qualitatively or semi-quantitatively.

25 In general, the organometallic catalyst(s) is (are) found in the final allophanate. The isocyanate monomers are separated from the converted compounds by distillation or by any other separation process (crystallization, extraction with gases in the critical or supercritical state, etc.) which can be carried out separately at the end of reactions a) and b) on the tricondensate polyfunctional isocyanate or the mixture of tricondensate polyfunctional isocyanates, on the one hand, and on the primary allophanate or the mixture of allophanates in the corresponding reactors or after the tricondensate polyfunctional isocyanate(s) and allophanate(s) have been
30 mixed together, i.e. on the allophanate/tricondensate
35

polyfunctional isocyanate mixture.

For the purpose of teaching by example (paradigm), in order to obtain compositions comprising an HDI trimer containing an isocyanurate unit (HDT), a viscosity of 700 mPa.s can be obtained by adding to a trimerization product HDI obtained by trimerization with a limited degree of conversion of the HDI of about 20%, having a viscosity of about 1200 mPa.s at 25°C, an amount of the allophanatation product such that the amount of primary HDI butyl allophanate in the final product is greater than or equal to about 3 per 100 g of final mixture, i.e. to about 15% by weight of primary allophanate per 100 g of final mixture.

Thus, when HDT having a viscosity of 2700 mPa.s at 25°C is used, the viscosity can be reduced to 1200 mPa.s at 25°C by adding an amount of allophanates of about 25% by weight relative to the weight of the final mixture in order to obtain a final concentration of about 15% by weight of primary allophanate.

Step d) is advantageously carried out by vacuum distillation of the HDI under the usual conditions.

The compositions obtained according to the invention contain the true tricondensate polyfunctional isocyanate(s) as well as heavy condensates, obtained by catalytic (cyclo)condensation of the starting isocyanate monomer(s) (first isocyanate(s) and optionally other monomers present), the primary monoallophanate and the heavy allophanate compounds such as di- and tri-allophanates, the second isocyanate(s) and optionally third isocyanate(s) (in the case of heteroallophanates) and the alcohol or the mixture of alcohols used for the carbamatation reaction, bis-allophanate, tris-allophanate and higher homologues. The allophanatation reaction is carried out such that the residual amount of carbamates (intermediate product not entirely converted) is small

(generally less than 20%, advantageously less than 10% and preferably less than 5%, by weight).

In general, the ratio:

5 Carbamate functions obtained from the alcohol molecule(s) used to make the allophanate

Allophanate functions obtained from the alcohol molecule(s) used to make the allophanate

10

is less than 0.5, preferably less than 0.2 and advantageously less than 0.1.

The process according to the present invention is particularly suitable for tricondensates comprising biuret units which generally generate high viscosities. However, when isocyanurate-based tricondensates are used, the amount of components comprising biuret units is preferably not high (less than 50%, preferably less than 25% and advantageously less than 10%).

15

20

However, even when the content of biuret units is between 0.5 and 5% by mass of the isocyanurate units, excellent results are still obtained.

25

30

In the absence of biuret units and especially when mixtures termed "low-viscosity", i.e. mixtures having a viscosity of not more than 1500 mPa.s, generally 1300 mPa.s, at 25°C, are used as starting isocyanurates, it is preferable, in order to obtain a significant reduction by adding a small proportion of allophanates (not more than about 30% by mass), to take allophanate mixtures whose viscosity is less than 500 mPa.s, preferably less than 200 mPa.s.

35

The composition according to the invention contains virtually no allophanates comprising tricondensate units, in particular isocyanurate obtained by cyclotrimerization of the starting isocyanate. Advantageously, it comprises

less than 10%, advantageously less than 8%, even more advantageously less than 5%, preferably less than 4% and more preferably less than 3%, and even more preferably less than 2%, it being possible for it to be as low as 1%, by weight, relative to the total weight of the composition.

In general, the compositions are characterized by an amount of allophanate compounds which is generally greater than 5% by weight and by a high G ratio defined below:

True tricondensate polyisocyanates, obtained from the condensation of three identical or different isocyanate molecules not modified with carbamate or allophanate

$$G = \frac{\text{Sum of the polyisocyanate molecules bearing at least one tricondensate function obtained from the condensation of three identical or different isocyanate molecules.}}{\text{Sum of the polyisocyanate molecules bearing at least one tricondensate function obtained from the condensation of three identical or different isocyanate molecules.}}$$

(The assembly of molecules bearing at least one tricondensate function is formed by the true tricondensate polyisocyanate compounds, the tricondensate polyisocyanate compounds in which at least one isocyanate function is engaged in a carbamate function, or an allophanate function or a heterocyclic function chosen from uretidine dione, isocyanurate, etc. functions).

The G ratio is generally greater than 0.3, preferably greater than 0.4 and advantageously greater than 0.5.

Such a composition is novel.

A subject of the invention is thus also a reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, the said composition being characterized in that it comprises less than 10%, advantageously less than

8%, even more advantageously less than 5%, preferably less than 4% and more preferably less than 3%, and even more preferably less than 2%, it being possible for it to be less than 1% of tricondensate allophanates relative to the total weight of the composition.

A subject of the invention is also a tricondensate polyfunctional isocyanate composition of significantly reduced viscosity, comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, the said composition satisfying at least one of the following conditions:

- a G ratio generally greater than 0.3, preferably greater than 0.4 and advantageously greater than 0.5,
- a primary allophanate/primary allophanate + true trimer weight ratio of between 2.5% and 99%, advantageously between 3% and 60% and preferably between 3.5% and 40%,
- the tricondensates are obtained from a tricondensation reaction for which the degree of conversion of the identical or different isocyanate monomer(s) into tricondensate polyfunctional polyisocyanates contained in the composition is greater than 8%, preferably greater than 10% and advantageously greater than 15%,
- at least 1% and not more than 99%, preferably at least 2% and not more than 75%, of biuret is present, these amounts being given on a weight basis.

Advantageously, it is preferable for the low-viscosity tricondensate polyfunctional isocyanate compositions comprising at least one true tricondensate polyfunctional isocyanate and at least one allophanate to satisfy the first two conditions, or even the first three conditions and better still the four conditions above.

In order to obtain low-viscosity compositions comprising tricondensate polyfunctional isocyanates from cycloaliphatic isocyanates, the process can be carried out in the same way as described above and a small amount of

solvent (generally less than 1/3, advantageously less than 1/4 and preferably less than 1/10 by weight, relative to the total weight of the composition) can optionally be added.

5 The compositions obtained according to the invention can be in the form of powders and can give a reduced viscosity on changing to the molten state, compared with products containing no primary allophanates.

10 The compositions in their various formulations, as aqueous or aqueous-organic solutions or in the form of powders, can also comprise identical or different protecting groups for the isocyanate functions. The isocyanate functions can be partially or totally protected. The ratio of free isocyanate functions to masked isocyanate
15 functions is chosen by a person skilled in the art as a function of the intended application.

20 The compositions obtained according to the invention can be used as aqueous formulations optionally with addition of formulation additives such as ionic or nonionic surfactants, or reversible or irreversible grafting onto the isocyanate functions of various polyoxyalkylene compounds such as polyethylene glycol derivatives or polyoxyethylenated amines.

25 These polyisocyanate compositions, containing isocyanate functions that are optionally partially or totally masked, can also give emulsions or suspensions as described in FR 2 703 357 and EP 691 993.

30 Polyols can also serve as formulating agents for these polyisocyanate compositions, to make aqueous solutions, emulsions or dispersions.

35 Similarly, these compositions can be used to prepare polyurethane compositions in powder or dissolved form or in aqueous or aqueous-organic solution, optionally masked with temporary and/or permanent masking agents. The choice of the polyol then depends on the intended

application.

The compositions which are the subject of the present invention are used with conventional coating additives, i.e. wetting agents, pigments, spreading agents, mar-resistance agents and any other compound known to those skilled in the art used in the applications mentioned above.

Among the many advantages offered by the invention, besides the reduced viscosity, mention may be made of the fact that the process according to the invention makes it possible to control the viscosity quickly and easily by adjusting the amount of one or other of the components (tricondensate polyfunctional isocyanates or allophanate(s)) of the mixture without being obliged to carry out a total synthesis, from the starting monomers and the alcohol.

In addition, for the same yield of allophanates relative to the process of the prior art, the degree of conversion of the monomer for a given viscosity is significantly higher.

The examples which follow illustrate the invention.

The NCO titre is expressed either as a % of NCO per 100 g of mixture or as moles of NCO per 100 g of mixture.

EXAMPLE 1: Preparation of low-viscosity (LV) HDT.

4584 g of hexamethylene diisocyanate (HDI) were introduced into a 6 litre three-necked reactor. The reaction medium is heated and stirred. 27.5 g of hexamethyl disilazane (HMDZ) are added at 113°C. The temperature of the reaction medium is then raised to 120°C. The temperature is maintained for 2 hours 15 minutes. The NCO titre measured at this stage is 1.069 mol of NCO per 100 g of mixture, which gives a degree of conversion of the HDI of 19.3%. The temperature of the reaction medium is reduced to 80°C and 16 ml of n-butanol are added to quench

the trimerization reaction. After reaction for one hour, the HDI monomer is removed by evaporation under vacuum to give an HDT product which has a viscosity of 1260 mPa.s at 25°C, a residual HDI content of less than 0.15% and a coloration of 5 hazen.

EXAMPLE 2: Preparation of a very low-viscosity HDI butyl allophanate.

4830 g of HDI are introduced into a 6-l reactor. 532 g of n-butanol are added over 50 minutes with stirring, while allowing the reaction temperature to rise to 108°C. 1.3 g of dibutyltin dilaurate are added at 125°C and the temperature is raised to 140°C. After reaction for 5 hours at about 140°C, the reaction is stopped by cooling. The NCO titre is 0.786 mol of NCO per 100 g of mixture. The HDI monomer is removed by evaporation under vacuum to give an HDI n-butyl allophanate with a viscosity equal to 140 cps and a titre of 0.405 mol of NCO per 100 g of product, i.e. 17% by weight of NCO per 100 g of mixture. The recovered yield of finished product is about 50% by weight. The amount of residual HDI is 0.05%. The amount of true primary HDI n-butyl allophanates is 57.8% by weight. The colour of the product is 10-15 hazen.

EXAMPLE 3: Medium-viscosity HDI butyl allophanate.

The process is performed in the same way as in Example 2, but with an NCO/OH ratio of 4.

The product has a viscosity of 600 mPa.s at 25°C, an NCO titre of 0.303, i.e. 12.7%, and an titre of residual HDI monomer of 0.1%. The recovered yield of finished product is 76.6% by weight. The composition of the product obtained is as follows, on a weight basis:

- primary HDI n-butyl allophanate
(mono-allophanate) : 30.6%
- butyl monocarbamate : 1%

- bis-allophanate : 25.7%
- tris-allophanate : 18.0%
- heavy isocyanates : 24.7%.

The colour of the product is 10-15 hazen.

5

EXAMPLE 4: Preparation of the low-viscosity mixture.

The mixture was prepared by applying the viscosity law given above.

10

A mixture containing 75% by weight of the composition obtained in Example 1 with 25% by weight of the composition obtained in Example 2 was prepared.

15

The characteristics of the products are obtained from analyses, quantified by infrared, of products separated on a separating column.

The characteristics of the mixture are given in the table below.

20

Table: Characteristics of an HDI butyl allophanate HDT mixture.

	Product of Example 1	Product of Example 2	Characteristics of the mixtures	
% of primary HDI n-butyl allophanate	0.7%	56.8%	14.45	14.45
% true (cyclo)tri- condensate	61%	0%	45.75	45
G ratio true (cyclo)tri- condensate/sum of the (cyclo)tri- condensates	0.69	0	0.69	0.68
Primary allophanate/ primary allophanate + true (cyclo)tri- condensate	1%		24%	23.8%
Biuret functions	6%		4.5%	4.5%
Viscosity (mPa.s at 25°C) (falling ball test)	1260	600	720	730

The increase in viscosity expressed by the ratio:
(viscosity of the product of Example 1 - viscosity of the
mixture)/viscosity of the product of Example 1
is equal to 42.9%.

5

EXAMPLE 5: Viscosities of mixtures according to the
invention as a function of the allophanate content.

HDT obtained according to Example 1 was mixed in
variable proportions with allophanates obtained according
to Example 2.

The viscosities are given in the attached figure.

EXAMPLE 6: Viscosities of HDB/HDI butyl allophanate
mixtures.

Hexamethylene diisocyanate biuret (HDB)/HDI butyl
allophanate mixtures were prepared as described above in
variable proportions and their viscosity measured.

The results are given in the table below:

Table: Characteristics of an HDB/HDI butyl
allophanate mixture.

HDB (% by weight)	HDI butyl allophanate (% by weight)	Viscosity (mPa.s at 25°C)	
		(1)	(2)
100	0	10 500	17 100
90	10	6 200	10 250
75	25	3 300	4600
50	50	750	1450

(1) HDB of standard viscosity (DC monomers \cong 40%)

(2) HDB of high viscosity

EXAMPLE 7: Synthesis of a low-viscosity norbornane
diisocyanate trimer (LV NBDT).

The product is synthesized according to the same
protocol as that described for Example 1, using 0.75 g of

hexamethyl disilazane per 100 g of norbornane diisocyanate (NBDI) and a reaction time of 3 hours at 120°C. The degree of conversion of the NBDI before the reaction is stopped is 20%.

5 The product purified of the excess monomer by distillation is a solid which has a measured viscosity of 4070 mPa.s at 25°C and at 80% solids content in n-butyl acetate and of 252 mPa.s at 25°C and at 70% solid content in n-butyl acetate.

10 **EXAMPLE 8:** Synthesis of a norbornane diisocyanate trimer (NBDT).

 The product is synthesized according to the same protocol as that described for Example 1, using 1.4 g of
15 hexamethyl disilazane per 100 g of norbornane diisocyanate (NBDI) and a reaction time of 3 hours at 120°C. The degree of conversion of the NBDI before the reaction is stopped is 26.4%. The product purified of the excess monomer by
20 distillation is a solid which has a measured viscosity of 13400 mPa.s at 25°C and at 80% solids content in n-butyl acetate.

EXAMPLE 9: Preparation of NBDT/low-viscosity HDI n-butyl allophanate compositions.

25 The compositions were prepared as indicated in the following table:

	Product of Example 8	Product of Example 9	Product of Example 2	Characteristics of the mixtures	
				60/40 Example 2/ Example 8	60/40 Example 2/ Example 9
% of composition by weight					
DC of HDI			50%		
DC of NBDI	20%	26.4%			
Residual HDI			0.05	0.03	0.03
Residual NBDI	0.61			0.25	
Viscosity in mPa.s at 25°C and at 100% solids content	solid*	solid**	140	4100	4500
Hazen colour	10-15	10-15	10-15	10-15	10-15
% of primary HDI n-butyl allophanate			56.8%	34	34
% true (cyclo)tri- condensate	74%	70%	0%	29.6	28
G ratio true (cyclo)tri- condensate/ sum of the (cyclo)tri- condensates	0.74	0.7	0	0.74	0.7
Primary allophanate / primary allophanate + true (cyclo)tri- condensate				53.5	55
Increase in viscosity				> 50%	> 50%

- * 4070 mPa.s at 25°C and at 80% solids content in n-butyl acetate
- ** 13400 mPa.s at 25°C and at 80% solids content in n-butyl acetate.

5

The increases in viscosity are significantly

greater than 50% given the fact that the products are solid and that the viscosity measured at 80% solids content is equivalent to or even greater than the viscosity of the two compositions.

5

EXAMPLE 10: Preparation of NBDT/HDT and low-viscosity HDI n-butyl allophanate compositions.

The compositions were prepared as indicated in the following table:

10

	Product of Example 8	Product of Example 1	Product of Example 2	Characteristics of the mixtures
% of composition by weight				45/15/40 Pdt1/Pdt2/Pdt8
DC of HDI		19.3	50%	
DC of NBDI	20%			
Residual HDI		0.15	0.05	0.07
Residual NBDI	0.61			0.25
Viscosity in mPa.s at 25°C and at 100% solids content	Solid*	1260	140	18500
Hazen colour	10-15	5	10-15	10-15
% of primary HDI n-butyl allophanate		0.7	56.8%	8.7
% true (cyclo)tri- condensate	74%	61	0%	57
G ratio true (cyclo)tri- condensate/sum of the (cyclo)tri- condensates	0.74	0.69	0	0.72
Primary allophanate/ primary allophanate + true (cyclo)tri- condensate				13
Biuret		6%		2.5%
Increase in viscosity				34%

- * 4070 mPa.s at 25°C and at 80% solids content in n-butyl acetate
- ** 13400 mPa.s at 25°C and at 80% solids content in n-butyl acetate.

5

The mixtures of the products of Examples 8 and 1 in a 52/48 ratio by weight has a viscosity of about 2800 mPa.s at 25°C and at 100% solids content.

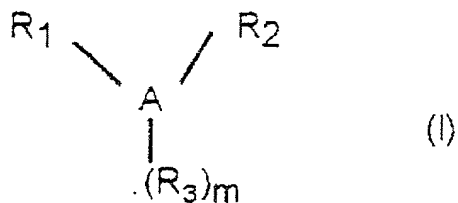
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The increases in viscosity are significantly greater than 50% given the fact that the products are solids and that the viscosity measured at 80% solids content is equivalent to or even greater than the viscosity of the two compositions.

CLAIMS

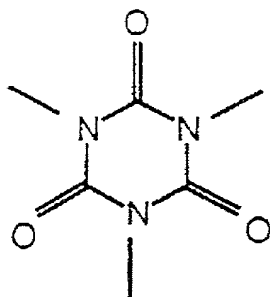
1. Process for preparing a tricondensate polyfunctional isocyanate composition, preferably comprising at least one isocyanurate and/or biuret group, which consists in adding to a tricondensate polyfunctional isocyanate, or to a mixture of different tricondensate polyfunctional isocyanates, obtained by (cyclo)condensation, in particular (cyclo)trimerization of one or more identical or different isocyanate monomers and optionally of another monomer, an allophanate of one or more identical or different isocyanates, or a mixture of different allophanates, the isocyanates or mixtures of isocyanate monomers used to prepare the polyfunctional isocyanate(s) being identical to or different from the isocyanate(s) or the mixture of isocyanates used to prepare the allophanate(s).

2. Process according to claim 1, characterized in that the tricondensate polyfunctional isocyanates correspond to the following general formula:



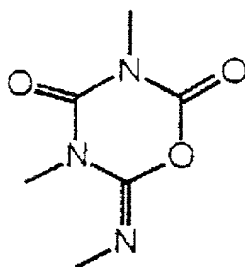
in which A represents

- an isocyanurate group of formula



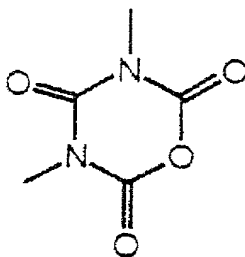
- one of its derivatives such as imino-oxadiazine-diones of the following formula:

5

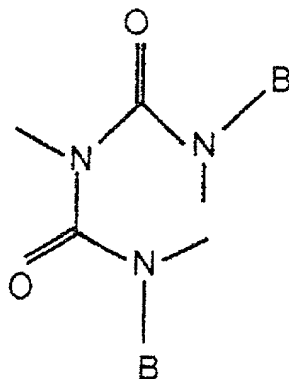


- one of its derivatives such as oxadiazine-triones of the following formula

10

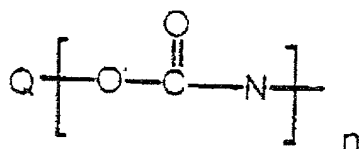


- a biuret group of formula



5 B being H or a hydrocarbon-based group, i.e. containing carbon and hydrogen as well as, optionally, other atoms (O, S, Si, etc.) preferably containing 1 to 20 carbon atoms; or

- a group of formula:



10 and in which R_1 , R_2 and R_3 , which may be identical or different, represent a hydrocarbon-based group, in particular an aliphatic, cycloaliphatic, heterocyclic or aromatic group, comprising a true or derived isocyanate function,

15 Q is a hydrocarbon-based group, preferably alkyl, as defined for R_1 to R_3 ,

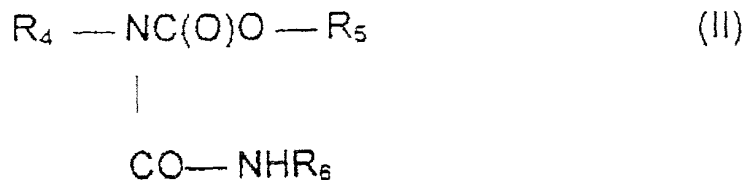
m is an integer from 0 to 2,

n is the integer 3 or 4.

20 3. Process according to either of the preceding claims, in which the tricondensate polyfunctional isocyanate composition comprises at least one true isocyanurate polyisocyanate.

25 4. Process according to any one of the preceding claims, in which the allophanates correspond to the general

formula II:



5 in which:

- R_4 and R_6 , which may be identical or different, represent a hydrocarbon-based group, in particular an aliphatic, cycloaliphatic, heterocyclic or aromatic group comprising a true or derived isocyanate function,
- 10 - R_5 representing an alkyl group, i.e. the residue of an alcohol compound after removal of the OH function.

5. Process according to any one of the preceding claims, characterized in that a mixture of allophanates comprising a primary allophanate, preferably containing
 15 about 1/4, advantageously about 1/3 and preferably about 2/5 (by mass) of primary allophanate(s), is added to the tricondensate polyfunctional isocyanates.

6. Process according to any one of the preceding claims, characterized in that the mixture of allophanates comprises mono-, bis- and tris-allophanates, in an amount
 20 advantageously of at least 2/3, preferably of at least 75% and even more preferably of at least 90%, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

7. Process according to any one of the preceding claims, characterized in that the amount of bis-allophanate represents up to 10% or even up to 20% of the total weight
 25 of the allophanate composition.

8. Process according to any one of the preceding claims, characterized in that the amount of tris-allophanates is less than or equal to 30%, advantageously
 30

20% and preferably 15% by weight, relative to the total weight of the composition.

9. Process according to any one of the preceding claims, characterized in that the ratio

5
$$\frac{\text{bis-allophanate functions} + \text{tris-allophanate functions}}{\text{mono-allophanate functions}}$$
 is equal to or greater than 0.1, and can be up to 0.3 or even 0.5.

10 10. Process for preparing a low-viscosity tricondensate polyfunctional isocyanate composition, comprising the following steps a) and b) in any order:

15 a) (cyclo)condensation, in the presence of a catalyst, of one or more identical or different first isocyanate monomer(s) until the desired degree of conversion is obtained;

20 b) reaction of one or more second isocyanate monomer(s) which are identical to or different from one another and identical to or different from the first isocyanate monomer(s), with an alcohol to form a carbamate, the reaction optionally being catalyzed, and simultaneous or subsequent reaction of the carbamate with one or more isocyanate monomer(s) which are identical to or different from the previous monomers, to give an allophanate or mixture of allophanates;

25 and steps c) and d) in any order:

c) mixing the reaction product from step a) with all or some of the reaction product from step b); and optionally

d) removing the isocyanate monomers.

30 11. Process according to claim 1 or 2, characterized in that the isocyanate(s) used for the (cyclo)condensation reaction is (are) identical to the isocyanate(s) used for the allophanatation reaction.

35 12. Process according to any one of the preceding claims, characterized in that the isocyanate(s) used for

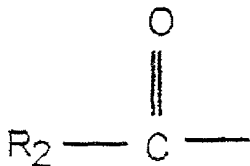
the allophanatation reaction and the isocyanate(s) used for the cyclotrimerization reaction satisfy at least one, advantageously two and preferably three of the following conditions:

- 5 - at least one, advantageously two, of the NCO functions are linked to a hydrocarbon-based skeleton via a saturated (sp^3) carbon;
- at least one, advantageously two, of the said saturated (sp^3) carbons bears at least one, advantageously two, hydrogen(s).
- 10 - all the intermediate carbons via which the isocyanate functions are linked to the hydrocarbon-based skeleton are saturated (sp^3) carbons which advantageously partially, preferably totally, bear a hydrogen, preferably two hydrogens.
- 15

13. Process according to any one of the preceding claims, characterized in that the alcohol is chosen from:

- aliphatic monoalcohols containing a C_1 - C_{10} linear chain;
- 20 - aliphatic monoalcohols containing a C_3 - C_{12} branch chain comprising not more than four secondary carbon atoms;
- diols containing a linear C_2 - C_{40} or branched C_3 - C_{40} chain;

of formula $R-[O-CH(R_1)-CH_2]_n-OH$, in which R_1 represents H or an alkyl group, preferably a C_1 - C_8 alkyl group, in particular methyl, or polyether, in particular $-CH_2OR_{10}$, R_{10} representing a hydrocarbon-based chain, in particular polyoxyalkylene, preferably polyoxyethylene, n is an integer preferably from 1 to 50, and R is a linear or branched C_1 - C_{20} alkyl group, or R is a group



with R₂ being a linear or branched C₁-C₂₀ alkyl group;

- silanols.

14. Process according to any one of claims 10 to 13, characterized in that the NCO/OH ratio in step b) is greater than 4, preferably greater than 6.

15. Process according to any one of the preceding claims, characterized in that at least about 25% by weight of the product from step b) is mixed with product from step a).

16. Reduced-viscosity tricondensate polyfunctional isocyanate composition comprising at least one true tricondensate polyfunctional isocyanate and at least one primary allophanate, the said composition being characterized in that it comprises less than 10%, advantageously less than 8%, even more advantageously less than 5%, preferably less than 4% and more preferably less than 3%, and even more preferably less than 2%, it being possible for it to go down to less than 1% of tricondensate allophanates relative to the total weight of the composition.

17. Reduced-viscosity tricondensate polyfunctional isocyanate composition, comprising at least one true tricondensate polyfunctional isocyanate and at least one allophanate, the said composition satisfying at least one, advantageously two, of the following conditions:

- a G ratio defined by:

True tricondensate polyisocyanates, obtained from the condensation of three identical or different isocyanate molecules not modified with carbamate or allophanate

$$G = \frac{\text{Sum of the polyisocyanate molecules bearing at least one tricondensate function obtained from the condensation of three identical or different isocyanate molecules.}}{\text{Sum of the polyisocyanate molecules bearing at least one tricondensate function obtained from the condensation of three identical or different isocyanate molecules.}}$$

Sum of the polyisocyanate molecules bearing at least one tricondensate function obtained from the condensation of three identical or different isocyanate molecules.

generally greater than 0.3, preferably greater than 0.4 and advantageously greater than 0.5,

- an allophanate/allophanate + true trimer weight ratio of between 2.5% and 99%, advantageously between 3% and 60% and preferably between 3.5% and 40%,

- the tricondensates are obtained from a tricondensation reaction for which the degree of conversion of the identical or different isocyanate monomer(s) into tricondensate polyfunctional polyisocyanates contained in the composition is greater than 8%, preferably greater than 10% and advantageously greater than 15%,

- at least 1% and not more than 99%, preferably at least 2% and not more than 75%, of biuret is present, these amounts being given on a weight basis.

18. Tricondensate polyfunctional isocyanate composition according to either of claims 16 and 17, characterized in that the mixture of allophanates comprises mono-, bis- and tris-allophanates in an amount advantageously of at least 2/3, preferably of at least 75% and even more preferably of at least 90%, by weight relative to the total weight of the allophanate composition after removal of the unreacted monomers.

19. Tricondensate polyfunctional isocyanate composition according to one of claims 16 to 18, characterized in that the amount of bis-allophanate represents up to 10%, or even up to 20%, of the total weight of the allophanate composition.

20. Tricondensate polyfunctional isocyanate composition according to one of claims 16 to 19, characterized in that the amount of tris-allophanates is less than or equal to 30%, advantageously 20% and preferably 15%, by weight relative to the total weight of the composition.

21. Tricondensate polyfunctional isocyanate composition according to one of claims 16 to 20,

characterized in that the ratio
bis-allophanate functions + tris-allophanate functions
_____ is greater than or equal to 0.1,
mono-allophanate functions

5 and can be up to 0.3 or even 0.5.

22. Tricondensate polyfunctional isocyanate
composition according to claim 16, comprising hexamethylene
diisocyanate biuret.

10 23. Use of a composition obtained according to any
one of claims 16 to 22, to prepare a coating.

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VISCOSITY OF A POLYISOCYANATE MIXTURE
HDT+HDI allophanate and butanol mixture

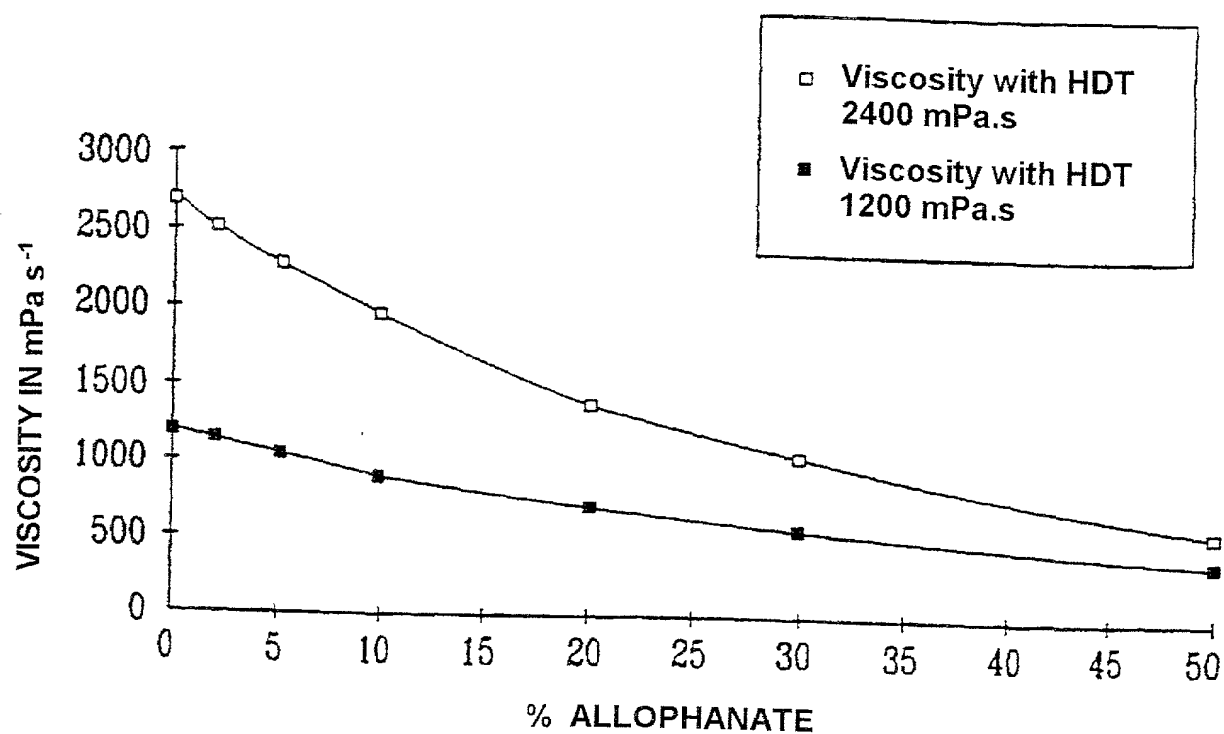


Figure 1

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to Provisional and PCT International Applications)

ATTORNEY'S DOCKET NUMBER

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

"Process for preparing low-viscosity tricondensate polyfunctional isocyanates".

the specification of which (check only one item below):

☒ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR99/00950

on April 21, 1999

and was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
FRANCE	98 05 170	April 24, 1998	X <input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number) _____

(Filing Date) _____

(Application Number) _____

(Filing Date) _____

ATTORNEY'S DOCKET NO

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

TOURNE 2 SUP

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONTINUED) (Includes Reference to Provisional and PCT International Applications)		ATTORNEY'S DOCKET NO
FULL NAME OF SOLE OR FIRST INVENTOR <u>CHARRIERE Eugénie</u>	SIGNATURE <u><i>Charriere</i></u>	DATE <u>August 28, 2000</u>
RESIDENCE 52, rue d'Inkermann - 69000 LYON France		CITIZENSHIP French
POST OFFICE ADDRESS 52, rue d'Inkermann - 69000 LYON France <u>FRX</u>		
FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>BERNARD Jean-Marie</u>	SIGNATURE <u><i>Bernard</i></u>	DATE <u>August 28, 2000</u>
RESIDENCE Route du Large - Saint-Laurent d'Agnay - 69440 MORNANT France <u>FRX</u>		CITIZENSHIP French
POST OFFICE ADDRESS Route du Large - Saint-Laurent d'Agnay - 69440 MORNANT France		
FULL NAME OF THIRD JOINT INVENTOR, IF ANY <u>REVELANT Denis</u>	SIGNATURE <u><i>Revelant</i></u>	DATE <u>August 28, 2000</u>
RESIDENCE 4, rue Bossuet - 69740 GENAS France <u>FRX</u>		CITIZENSHIP French
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FULL NAME OF FOURTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF NINTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		